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A SUMMARY AND EVALUATION OF AQUATIC ENVIRONMENTAL DATA IN RELATION TO ESTABLISHING WATER QUALITY CRITERIA FOR MUNITIONS UNIQUE COMPOUNDS

NITROCELLULOSE

FINAL REPORT

J.H.SULLIVAN, JR., H.D.PUTNAM, M.A.KEIRN,
B.C.PRUITT, JR. AND J.C.NICHOLS

OCTOBER, 1978

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The purpose of this report is to review the effects of nitrocellulose on the aquatic environment and to recommend water quality criteria for the protection of aquatic organisms.

Nitrocellulose is a fibrous, cotton-like, white solid consisting of chains of linked glucoside units in which the hydroxyl groups of the glucose subunits have reacted to form nitrate esters. The chemical formula is

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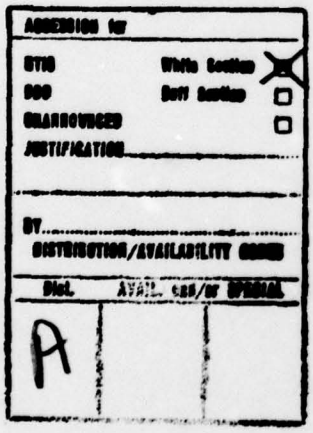
approximately $[C_6H_7O_2(OHO_2)_3]_n$; the molecular weight depends on chain length. Nitrocellulose is insoluble in water.

Four species of invertebrates and four species of fish were unaffected by nitrocellulose concentrations as high as 1000 mg/1. The fish testing included exposure of fathead minnows at several life stages (egg through 60 day old fry). Chronic exposure of the midge to sediment containing nitrocellulose concentrations as high as 540 mg/kg over two generations showed no significant effects on survival or adult emergence.

Four species of algae were exposed to nitrocellulose concentrations up to 1000 mg/1. Three species were unaffected and the fourth, Selenastrum capricornutum, showed a 96-hr. EC50 of 731 mg/1. This species is very sensitive to light intensity and it was concluded that the response noted was due to light reduction caused by the suspended nitrocellulose particles.

The particulate nature of nitrocellulose wastes, the compound's relative insolubility in water, as well as its observed ability to attenuate light transmission through a suspension medium, indicate that current EPA water quality criteria for solids and turbidity are sufficient to provide for safe levels of nitrocellulose in the aquatic environment. These criteria (EPA 1976) suggest for the protection of freshwater fish and aquatic life:

> Settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life.



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A Summary and Evaluation of Aquatic Environmental Data in Relation to Establishing Water Quality Criteria for Munitions Unique Compounds

Nitrocellulose

FINAL REPORT

October 1978

by

J. H. Sullivan, Jr.
H. D. Putnam
M. A. Keirn
B. C. Pruitt, Jr.
and J. C. Nichols

Supported by

U.S. Army Medical Research and Development Command
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J. Gareth Pearson, Project Officer

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I. Introduction

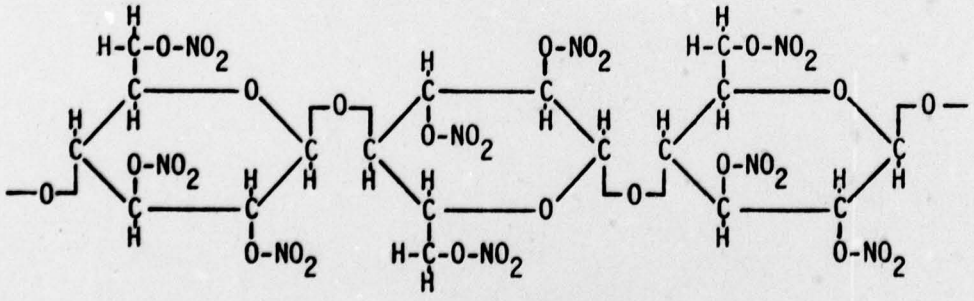
Since the early part of the 1970's the U.S. Army Medical Research and Development Command has been supporting research to determine the environmental hazards associated with waste discharges of its munitions industry. The objective of these studies has been to formulate water quality criteria for safe levels of munitions by examining effects on mammalian and aquatic species and communities. The data base for the target compounds has been under periodic review to determine the necessary requirements for final water quality criteria.

The purpose of this report is to review the effects of nitrocellulose on the aquatic environment and to recommend water quality criteria for the protection of aquatic organisms. This substance forms the basic component for many military propellants and therefore constitutes an important part of munitions manufacture in this country. Wastes which are discharged from nitrocellulose production contain various concentrations of trinitrated cellulose fibers. The impact of these particulates has been examined by assessing fish, invertebrate, and algal toxic response by conducting laboratory bioassays. In addition, field investigations have documented the response of selected aquatic communities to this substance.

The recommended acute and chronic safe levels for water were developed from the existing data base using the guidelines of the Toxic Substances Control Act of 1976 (PL 94-469), APHA (1975), National Academy of Sciences (1973), and EPA (1976, and 1978) methodology. The latter three documents contain the strategy necessary to provide application factors for predicting environmentally safe levels based on laboratory bioassays.

II. Chemical and Physical Properties

Nitrocellulose, or cellulose trinitrate, is a fibrous, cotton-like, white solid (specific gravity 1.66) consisting of chains of β, 1 → 4-linked glucoside units in which the hydroxyl groups of the glucose subunits have reacted to form nitrate esters. The chemical formula is approximately $[C_6H_7O_2(ONO_2)_3]_n$; the molecular weight depends on chain length. The chemical structure of a section of nitrated glucoside chain is shown below:

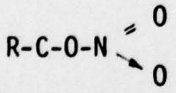


Typical molecular weights for cellulose, the parent compound of nitrocellulose, range from 1.0×10^5 to 2.5×10^6 (Alexander 1977) and consist of from 2,000 to 10,000 glucose units per molecule. Nitrocellulose is extremely flammable and has a flash point of 12.8°C. (Hawley 1977). The melting point range is 160°- 170°C - the autoignition temperature.

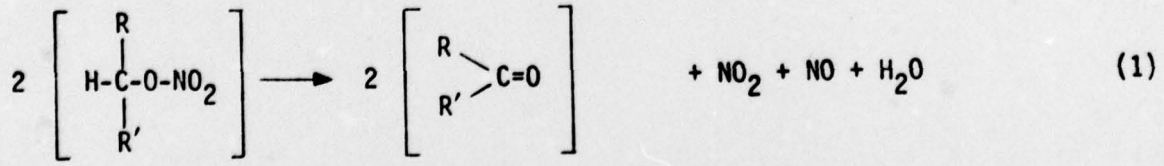
"Guncotton", military grade cellulose nitrate contains 13.5 percent nitrogen (Patterson et al. 1976) and is the most highly nitrated form. Theoretically mononitrated, dinitrated, and trinitrated cellulose contain 10.9 percent N, 11.1 percent N, and 14.1 percent N, respectively. "Guncotton" is essentially fully nitrated and therefore can be considered to be a crude cellulose trinitrate contaminated by traces of less completely nitrated esters. The general properties of cellulose trinitrate are summarized in Table 1.

The nitrate esters in general are soluble in esters, aldehydes, and ketones. The more completely nitrated a cellulose is, however, the smaller the range of materials in which it is soluble. The less nitrated forms of cellulose nitrate are also very soluble in methanol, benzene, toluene, and mixtures of ether and ethanol. These compounds (pyroxylin; 8-12 percent N and pyrocellulose (12.5 percent N) are forms of collodion and are used chiefly as lacquers, ink bases, as filter membranes, and in veterinary medicine for wound closure. Cellulose trinitrate is insoluble in water, ethanol, ethyl ether, and benzene but completely miscible in acetone, methyl-ethyl ketone, tetrahydrofuran, as well as nitrobenzene, ethyl-, butyl-, and amyl acetates. Cellulose trinitrate is also sparingly soluble in 2:1 ethyl ether:ethanol mixtures. (Mark et al. 1965; Hawley, 1977).

Reactivity. Poly-nitrated alcohols as a group owe their chemical instability and brisance to the configuration of the nitrate bond:



where the $O\text{-}NO_2$ moiety is coplanar but perpendicular to the carbon atom. Proximity of several nitrate groups sets up carbon-carbon and carbon-oxygen bond stresses. Explosive decomposition releases nitric oxide and nitrogen dioxide to yield an aldehyde or ketone of the parent alcohol (Boschan et al. 1955):



$$+ NO_2 + NO + H_2O \qquad (1)$$

Very little energy input is required to initiate this reaction, however

TABLE 1

SUMMARY OF GENERAL PROPERTIES
OF CELLULOSE TRINITRATE

Name	Cellulose trinitrate; nitrocellulose; guncotton	
Molecular weight	Variable	
Empirical formula	$[C_6H_7O_2(ONO_2)_3]_n$	
Color	Whitish	
Physical state	Fibrous solid; specific gravity 1.66	
Percent nitrogen	14.1	approximate, depends on processing and chain length
carbon	24.3	
oxygen	59.2	
hydrogen	2.4	
Solubility characteristics	Generally soluble in ketones and esters; soluble in acetone in all proportions; soluble in methyl-ethyl ketone, nitrobenzene, tetrahydrofuran, and ethyl-, butyl-, and amyl-, acetate. Insoluble in water, ethanol, benzene and most other solvents. Sparingly soluble in 2:1 ethyl ether:ethanol.	

the massive energy output from the first step generally results in complete oxidation of the organic moiety to gaseous products. In the case of cellulose trinitrate, the overall reaction yields the following for each pair of subunits:

$$[C_6H_7O_2(ONO_2)_3]_2 \rightarrow 11\ CO + 7\ H_2O + 2\ N_2 + 2\ NO + CO_2 \qquad (2)$$

The nitrogen in this compound is oxidized only to the neutral N° or N^{+2} state rather than N^{+4} as NO_2 (Wibaut, 1951).

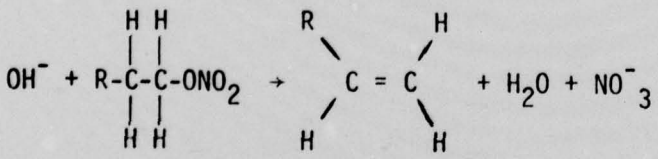
Nitrocellulose reacts as above and forms a basic component for all military propellants; single base, double base (combined with nitroglycerin), and triple base (combined with nitroglycerin and nitroguanidine), (Glennon et al. 1977). Tew and Jaffe (1973) cited a 1907 paper by Malenovic which stated that nitrocellulose in contact with decomposing organic matter was itself degraded. Nitrocellulose, however, is resistant to biological degradation and is a persistent compound in the environment. Alexander (1978) and Reese (1978) have suggested that cellulose triacetate and cellulose trinitrate are resistant to enzymatic attack. Also, according to Bluhm (1976), direct biodegradation of nitrocellulose is not feasible, however, alkaline hydrolysis yields material which can be decomposed by microbial activity. Nitrocellulose therefore can be characterized as being persistent in the environment unless chemically altered.

Basic hydrolysis at 90°-95°C (Bluhm 19[illegible]ied organic and inorganic products which gave infrared spectra suggesting [illegible]presence of hydroxy-carboxylic acids, as well as "nitro" groups. Mass spectroscopy suggested that fragments with molecular weights in the range of 104 to 118 form major components of the hydrolysate. Boschan et al. (1955) suggest three general mechanisms of basic hydrolysis:

Nucleophilic substitution:

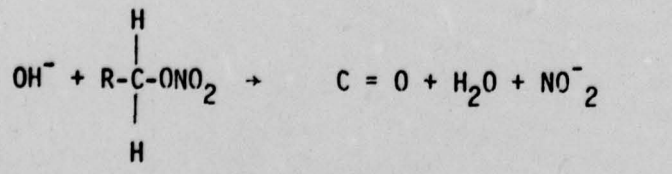
$$OH \quad OH^- + RONO_2 \rightarrow ROH + NO_3^- \qquad (3)$$

Elimination of β-hydrogen:



(4)

Elimination of α-hydrogen:



(5)

These three reactions are bimolecular, however hydrolysis would tend to show first order kinetics in neutral aqueous systems where H_2O is a primary reactant. Basic hydrolysis would tend to have more second order characteristics. In the case of cellulose trinitrate, reactions with water do not proceed to an appreciable extent.

Tew and Jaffe (1973) summarized an extensive volume of literature dealing with the adsorptive capacity of nitrocellulose for biologically important macromolecules. Nitrocellulose strongly adsorbs and concentrates DNA and various RNA molecules from solution, and adsorbs proteins and polypeptides under various conditions. Proteins with an uncoiled structure or of molecular weight greater than 10^5 are strongly bound. Denatured proteins are also strongly sorbed, especially under acidic conditions. The property of sorption of macromolecules is common to most particulate organic matter in the aquatic environment (Paerl 1974).

Manufacturing Wastewater Characteristics. Nitrocellulose is currently produced at Radford Army Ammunition Plant (RAAP), Radford, Virginia (Patterson et al. 1976). Three additional, inactive plants are capable of manufacturing this product. These are Badger, Iowa, and Sunflower Army Ammunition Plants. Studies of the environmental fate and effects of nitrocellulose discharges into the receiving waters for both active plants are described in Section IV.

The manufacturing processes at BAAP and RAAP have been summarized by Patterson et al. (1976). Nitrocellulose is produced by treating cotton linters or wood pulp with mixed nitric and sulfuric acids. The crude product is subjected to prolonged treatment in dilute H_2SO_4, cut and beaten to control fiber length, then washed and poached to remove residual acid. A large amount of water is required for the latter stages of the process, much of which is discharged to the environment. Wastewater contains fine nitrocellulose particles, high NO_3^- and $SO_4^=$ concentrations, and generally has low pH due to acid discharge. Table 2 summarizes the characteristics of process wastewater from manufacturing. In addition to the main waste flow, a small volume of discharge results from solvent recovery operations (see also Table 2). Nitrocellulose concentration ranges in combined, unsettled wastewater were reported to be approximately 200 to 500 ppm.

Treatment of the wastewater consists of settling, recovery of the suspended nitrocellulose, and neutralization. Subsequent to the Patterson report (Patterson et al. 1976), RAAP has added centrifugation to remove and recover nitrocellulose fines. The effluent contains organic material and suspended solids, mostly fine nitrocellulose fibers, along with high dissolved solids, nitrates and sulfates. Typical nitrocellulose fines have been characterized by Helton (1976) from two samples of wastewater from RAAP prior to the installation of centrifuges. Nearly all of the material was larger than 5μ effective size based on the ability to pass through sized membrane filters. Table 3 summarizes this information for the various particle size classes. The average particle diameter was approximately 31μ for ten particles randomly chosen from the size classes with particle lengths greater than 5μ. The material studied was derived from cotton linters. The data suggest that suspended solids below 0.8μ effective

TABLE 2

TYPICAL CHARACTERISTICS OF NITROCELLULOSE MANUFACTURING WASTEWATER

Parameter	Discharge Range	
	Process Water	Solvent Recovery
Flow (MGD)	2.96-7.07	0.0086-0.021
Production (Ton/Day)	29-70	19.14-20.71
Gallons (H_2O/Ton)	45,000-157,000	---
pH	0.9-12.4	7.1-7.4
NO_2/NO_3-N (mg N/l)	190-648	3.0
Kjeldahl-N (mg N/l)	0.19-6.84	2.0
Acidity(mg $CaCO_3$/l)	0.07	7.0-7.3
Alkalinity (mg $CaCO_3$/l)	2.83	246-372
Dissolved Solids (mg/l)	47.8-9880	34.7-2695
Sulfate (mg SO_4/l)	500	---
Suspended Solids (mg/l)	68 - 312	7.17-2545
BOD (mg/l)	1.17	44.7-295
COD (mg/l)	80-784	104

Source: Patterson et al.(1976).

TABLE 3

CHEMICAL AND PHYSICAL CHARACTERISTICS OF FINE NITROCELLULOSE PARTICLES

Nitrocellulose Particle Size Range[a] (μ)	Distribution of Material by Weight (%)	Fiber Length (Average) (μ)	Molecular Weight		Percent Nitrated[b] (%)
			Number Average	Weight Average	
>88	66	600	37,200	165,000	91 ± 2
>44 -<88	23	200	54,000	158,000	95 ± 2
>5 -<44	11	20	7,700	167,000	82 ± 2
>0.8 -<5	<0.1	--	8,690	110,000	82 ± 2
>0.2 -<0.8	<0.1	--	--		29 ± 1
<0.2	<0.1	--	--		24 ± 1

(a) Effective particle size indicates the ability of the material to pass through filters of designated pore sizes.

(b) 100% nitration = 3 NO_3^- per glucose unit.

Source: Helton (1976).

size contain significant portions of nonnitrated cellulose and other materials. Particles greater than 44μ are mostly nitrocellulose. Chemical, elemental, and differential thermal analyses also suggest that most of the particles greater than 0.2μ contain significant nitrate ester functional groups and that particles >44μ are fully nitrated. The waste discharge rate, settling time, physical characteristics of the outfall, the type of starting material (i.e. wood pulp or cotton), and many other factors influence the percent by weight of the nitrocellulose mass discharge in each particle size class.

II-A. Analytical Methods: Environmental Monitoring

Rosenblatt et al. (1973) reviewed the analytical chemistry of nitrocellulose and concluded that the following methods commonly employed for the determination of nitrocellulose lack either sensitivity or specificity at the low levels found in the environment:

1. Ferrous-titaneous titration
2. Ferrous sulfate titration
3. NO_2 gas liberation
4. Analysis of NH_3 after reduction by Devarda's alloy
5. Transnitration of salicylate or citrate followed by ferrous-titaneous titration.
6. Chromous chloride-ferric ammonium sulfate micro-determination.

The most effective method for detection of low levels of nitrocellulose in the environment is the colorimetric method based on hydrolytic liberation of nitrite (Rosenblatt et al. 1973). Nitrite is liberated by OH^- from acetone solutions of nitrate esters by the reaction discussed in the previous section. The resulting NO_2^- is then diazotized with either α-naphthylethylenediamine hydrochloride or α-naphthylamine and the absorbance of the solution determined at 520 to 530 nm. The reaction itself is not specific for nitrocellulose; however, the insolubility of this compound in water allows quantitative separation from NO_2^-, NO_3^-, and other soluble nitrate esters or nitrocompounds in mixed wastewater by filtration or dialysis. The scheme outlined below can detect 1 mg/l or less of nitrocellulose in water in a sample size of 100 ml. Filtration of larger sample sizes could extend detection limits. Rosenblatt and Small (Rosenblatt et al. 1973) have successfully adapted the above procedure to the Technicon Autoanalyzer.

Determination of nitrocellulose in sediment is more complicated. Each of the available methods has several drawbacks. One method outlined by Cooper et al. (1974) uses the above procedure to detect nitrocellulose in acetone or ethyl acetate extracts of dried sediment. The sediment is treated overnight in a Soxhlet extractor. This procedure also extracts other organic nitrate esters and nitro-compounds from the sediment matrix. The analysis is not therefore necessarily specific for nitrocellulose although it is sensitive to as little as 0.5 mg/kg of nitrate ester in sediment systems. The second procedure used by Bentley et al. (1977) to

measure nitrocellulose concentrations in artificial sediment systems, was developed to determine nitrocellulose in mixtures of munitions compounds (McDougall 1975). This procedure lacks sensitivity, however, since the minimum detectable concentrations on a 10 g sediment sample is 140 mg/kg. The basis of this latter test is acetone extraction of the nitrate ester and determination of the NO_3^-. Nitrate present in the extract oxidizes ferrous iron to ferric iron after treating the extract with acetic acid, ferrous sulfate in sulfuric acid, and sodium sulfite. The resulting yellow color is quantified at 500 nm.

III. Toxicological Aspects

Fine, insoluble fibers of nitrated cellulose are a component of wastewater discharge from the manufacturing of nitrocellulose and result in concentrations of a few ppm in the water and up to nearly 300 ppm in the sediments of receiving systems. The resistance of this compound to biodegradation suggests that its toxicity to aquatic life should be defined. Bentley et al. (1977) investigated the acute toxicity of nitrocellulose to algae and fish and the acute and chronic toxicity to invertebrates. No other toxicological research has been reported for the effects of nitrocellulose on aquatic organisms. Ellis et al. (1976) have defined the effects of nitrocellulose on dogs, rats, and mice and concluded that nitrocellulose is not absorbed in the digestive tract of mammals. The results of toxicity bioassays to aquatic organisms have been summarized in Table 4.

Microorganisms. Bentley et al. (1977) investigated the toxicity of nitrocellulose for four species of algae: Microcystis aeruginosa and Anabaena flos-aquae (two cyanophytes); Navicula pelliculosa (a diatom); and Selenastrum capricornutum (a chlorophyte) using the procedures outlined by the EPA (Algal Assay Procedure: Bottle Test, EPA 1971). Chlorophyll a and either cell numbers (S. capricornutum, M. aeruginosa, and N. pelliculosa) or optical density (A. flos-aquae) were used as the response parameters in duplicated challenge concentrations and controls. Reduced growth was correlated with increased nitrocellulose concentrations after 96 hours exposure for all species tested. The averaged percent inhibition data relative to controls, converted to probits (probability units) were plotted against the logarithm of normal concentrations to determine a 96-hour EC50. Responses of both blue-green algae and the diatom indicated that the 96-hour EC50 was greater than 1000 mg/l nitrocellulose. The 96-hour EC50 for S. capricornutum was estimated as 579 mg/l with a 95 percent confidence interval of 138 to 2400 mg/l nominal nitrocellulose concentrations.

A linear regression analysis of the Bentley et al. (1977) mean response data for Selenastrum capricornutum, the most sensitive algal species tested, generated a 96-hour LC50 of 731 mg/l with a 95 percent confidence interval of 475-1039 mg/l. The growth of this algal species was estimated by this same technique to be significantly ($p < 0.05$) reduced compared to controls at concentrations as low as 114 mg/l.

Aquatic Invertebrates. Acute toxicity studies conducted by Bentley et al. (1977) demonstrated that nitrocellulose was not acutely toxic to four

TABLE 4

ACUTE TOXICITY (EC50 OR LC50) OF NITROCELLULOSE TO SELECTED FRESHWATER ORGANISMS UNDER STATIC BIOASSAY CONDITIONS

Organism	Test Duration (hrs)	Concentration (mg/l)
Microorganisms (EC50)		
Cyanophytes (blue-green algae)		
Microcystis aeruginosa	96	>1000
Anabaena flos-aquae	96	>1000
Chrysophyte (diatom)		
Navicula pelliculosa	96	>1000
Chlorophyte (green alga)		
Selenastrum capricornutum	96	731
Invertebrates (EC50)		
Water Flea		
Daphnia magna	48	>1000
Amphipod		
Gammarus fasciatus	48	>1000
Isopod		
Asellus militaris	48	>1000
Midge		
Chironomus tentans	48	>1000
Vertebrates (LC50)		
Bluegill		
Lepomis macrochirus(1)	96	>1000
Rainbow Trout		
Salmo gairdneri	96	>1000
Channel Catfish		
Ictalurus punctatus	96	>1000
Fathead Minnow		
Pimephales promelas(2)	96	>1000

(1) Also tested to determine the effects of pH, hardness, and water temperature on toxicity.

(2) Selected life stages of this organism were tested to determine acute toxicity; eggs, 1-hour old fry, 7-day old fry, 30-day old fry, and 60-day old fry.

Source: Based on the data of Bentley *et al*. (1977).

species of macroinvertebrates after 48 hours exposure to concentrations as high as 1,000 mg/l in the water column. These were the water flea (Daphnia magna), the amphipod (Gammarus fasciatus), the isopod (Asellus militaris) and the midge (Chironomus tentans). Chronic exposure of the midge to sediment containing nitrocellulose concentrations as high as 540 mg/kg over two consecutive generations failed to produce significant effects on survival or adult emergence.

Fish. The four species, the bluegill (Lepomis macrochirus); the rainbow trout (Salmo gairdneri); the channel catfish (Italurus punctatus); and the fathead minnow (Pimephales promelas) were unaffected by nitrocellulose concentrations as high as 1,000 mg/l (Bentley et al. 1977) under static bioassay conditions. Toxicity tests conducted with bluegills were run with various temperatures (15°, 20°, and 25°C); hardness levels (35, 100, and 250 mg-$CaCO_3$/l), and pH (6.0, 7.1, and 8.0) to investigate the possible effects of variable water quality. None of these water quality variations produced mortality. Several life stages of the fathead minnow (egg through 60 day old fry) were tested to determine potential acute effects. None of the juvenile fish or eggs were affected at up to 1,000 mg/l nitrocellulose.

Adequacy of the Data Base. The present data appear to define the general toxicity of nitrocellulose to aquatic organisms. None of the fish and invertebrates tested exhibited adverse effects to concentrations of nitrocellulose as great as 1,000 mg/l. The algae were adversely affected at high concentrations. One alga was calculated to have a nitrocellulose 96-hour EC50 of 731 mg/l. These concentrations are higher than those encountered in the receiving waters at the nitrocellulose manufacturing plants. For these reasons, further aquatic toxicology studies are not indicated.

Mechanisms of Toxicity. There are no published data defining biochemical mechanisms by which nitrocellulose can adversely affect aquatic organisms. Bentley et al. (1977) offered no hypotheses regarding the reduced growth response of the algal species at high nitrocellulose concentrations compared to controls. There is indirect evidence, however, suggesting that the probable mechanism by which nitrocellulose suspensions affect algal growth response is due to reduction of light intensity. Growth effects were limited to concentrations above 100 mg/l. Suspensions of this mass of insoluble nitrocellulose fibers represent a very significant turbidity. The Selenastrum was the most sensitive test species followed by the Microcystis and the Navicula. These two organisms were roughly similar in their sensitivity. Anabaena was the least affected of the four. Figure 1 presents data which show that the response of Selenastrum capricornutum, Microcystis aeruginosa, and Anabaena flos-aquae to variations in light intensity. These data (EPA 1971) indicate that Selenastrum is much more sensitive to light intensity in the first 96 hours (4 days) of growth than either Anabaena or Microcystis. The tests shown in this figure were run using the same algal strains and under similar cultural conditions to the toxicity tests reported in Bentley et al. (1977). The EPA (1971) bioassay procedure requires that Selenastrum be cultured at 400 foot candles. The other two species are cultured at 200 foot candles. The diatom (Navicula

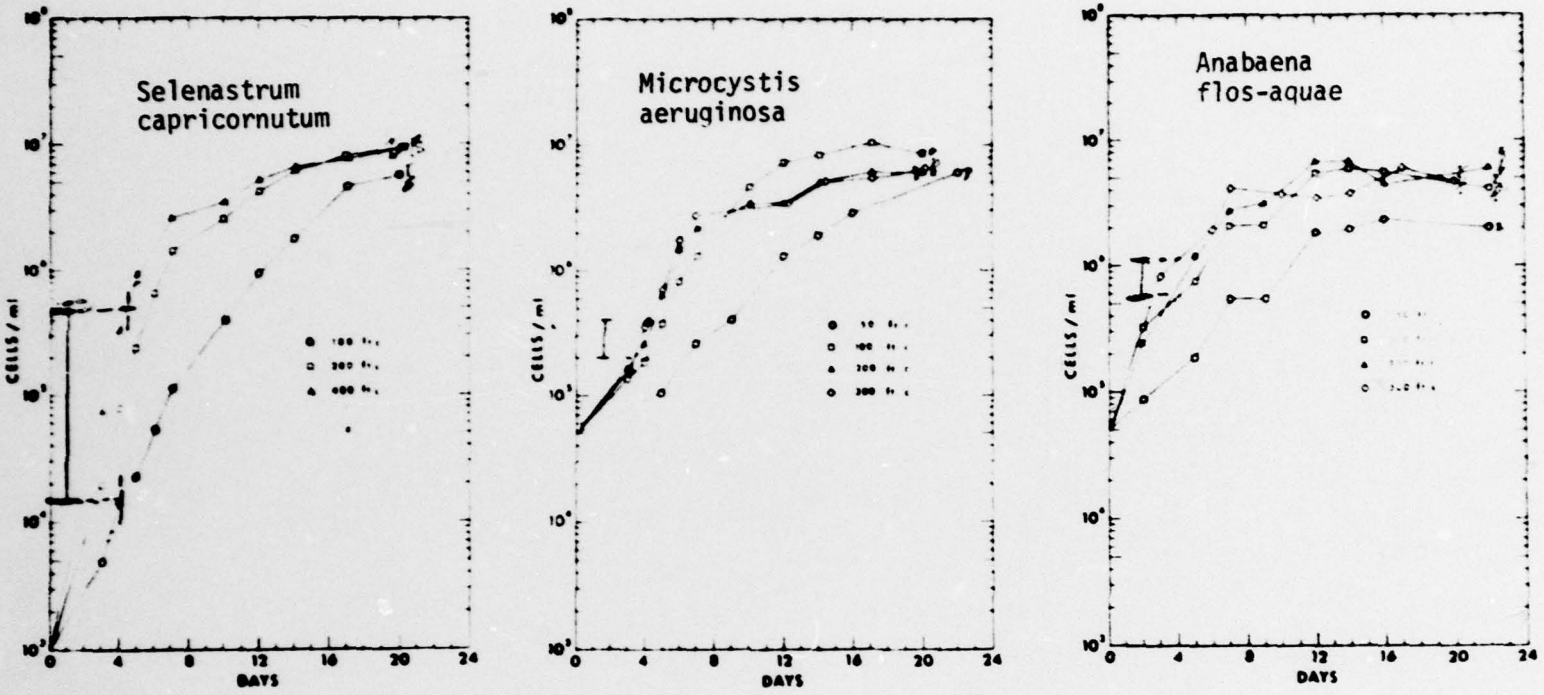


FIGURE 1. EFFECT OF LIGHT INTENSITY ON THE GROWTH RATE OF THE ALGAL TEST SPECIES. Source: EPA (1971)
The (I) represents the difference between the 100 foot candle and 400 or 300 foot candle response at 4 days (96 hours).

pelliculosa) has not been studied extensively under these cultural conditions, therefore its response to light intensity is unknown (Greene 1978). In the turbid suspension which results from the addition of 100 to 1,000 mg/l nitrocellulose in water, significant reductions in the growth response would be expected for the algal species tested based on their known response to light intensity. A reduction in light level from 400 to 100 foot candles produced more than an order of magnitude reduction in growth response for Selenastrum capricornutum. This is much greater than the effect on this species in the toxicity test, however, the extent to which the suspension of nitrocellulose would lower effective light intensity in the culture flask is not known.

The aquatic field studies (Section IV) in general attribute the environmental impact of nitrocellulose wastewater to factors other than nitrocellulose. Sediment characteristics, however, were affected. In general, process wastewater contains large amounts of COD, but little BOD (Table 2). The settled waste discharges consist of the finer particles such as those characterized by Helton. These particles would be carried to quiescent waters where over a period of time they would bury the existing substrate. This physical effect may permanently alter the benthic community structure. Although the actual cellulose trinitrate fibers resist degradation, other organic material and incompletely nitrated cellulose particles trapped in the matrix could have an oxygen demand and create anaerobic conditions.

IV. Environmental Fate and Effects

Wastewater from the manufacture of nitrocellulose is neutralized, then settled, centrifuged, and/or screened to recover nitrocellulose fibers. Approximately 50 to 100 ppm of fine nitrocellulose particles pass through the treatment process and are discharged into receiving water systems (Rosenblatt et al. 1973). These insoluble particles may persist in the water column in turbulent systems; however, due to its particulate nature, insolubility, and specific gravity, the material appears to accumulate in receiving water sediments. Once in the environment, nitrocellulose is extremely stable and may persist for an indefinite period of time.

Rosenblatt et al (1973) predicted maximum concentrations which would occur downstream of the discharges at BAAP and RAAP based on average flow and waste discharge conditions. Discharges from BAAP flow into the impounded Wisconsin River approximately 80 miles from its confluence with the Mississippi. Rosenblatt et al. (1973) predicted concentrations of approximately 0.6 ppm in the Wisconsin River and 0.15 ppm in the Mississippi at the confluence. At RAAP, wastewater is discharged to the New River which flows into the Kanawha River and on into the Ohio River above Gallipolis, Ohio. Nitrocellulose concentrations of 1 ppm were predicted 30 miles downstream at Bluestone Lake at the Virginia-West Virginia border. Concentrations were predicted to be less than 0.1 ppm at the confluence with the Ohio (~80 miles). The environmental impact of wastewaters from both of these plants has been studied (Cooper et al. 1974; Huff et al. 1975; Stilwell et al. 1976; and Weitzel et al. 1976). In addition, the impact of nitrocellulose in a loading facility discharge was studied by Cooper et al. (1974) at Lake City Army Ammunition Plant (LCAAP), Blue Springs, Missouri.

At this facility, discharges flow into the Little Blue River via a drainage ditch.

Wastewaters from RAAP increased solids, $SO_4^=$, total organic carbon, and nitrogen levels in the New River resulting in impact on the macrobenthos and fish populations. None of the effects could be directly attributed to munitions compounds, however. Weitzel et al. (1976) focused primarily on the effects of nitroglycerin and Huff et al. (1975) did not attempt to detect nitrocellulose, therefore, no documentation of nitrocellulose levels exists for the New River.

At LCAPP, low levels (0 - 4.6 ppm) of nitrocellulose were detected in the water and sediment of the drainage ditch. Other compounds, nitroglycerin and pentaerythritol tetranitrate, were also discharged and may have formed a component of the concentrations detected. Alterations in the periphyton and benthic invertebrates were found within the ditch and in the Little Blue River. Discharges of high concentrations of chloride, sulfate, copper and antimony also occurred. The biotic effects therefore were not thought to result from munitions compounds themselves.

The effects of nitrocellulose on aquatic life at BAAP were investigated by Cooper et al. (1974) and by Stilwell et al. (1976). Nitrocellulose was discharge through an inoperative industrial treatment plant into a series of three settling ponds. Relatively high levels of NO_2/NO_3, sulfate, and chloride were discharged into the receiving waters along with the nitrocellulose. Nitrocellulose was detected in the receiving waters below the discharge at concentrations of <1.0 to 12.1 mg/l, and in the receiving sediments at concentrations of 17.8 to 296 mg/kg. Standing crop, diversity, chlorophyll a, and biomass of periphyton and phytoplankton were depressed. Stilwell et al. (1976) attributed the effects to something other than nitrocellulose, such as intermittent high chlorine concentrations in the sanitary effluent also discharged to the system. Discussion of the waste neutralization process at BAAP by Patterson et al. (1976) suggests an alternative explanation for the extreme stress on population in the upper reaches of the receiving system. Inadequate control of neutralization processes resulted in frequent pH fluctuations of 5 to 10 pH units. The stresses in the lower receiving system were believed to be due to anaerobic conditions in the sediments and physical habitat alteration from the nitrocellulose wastewater discharges and not to nitrocellulose toxicity (Stilwell et al. 1976).

In general, the field studies fail to define any clear cut toxicity of nitrocellulose to aquatic organisms. The work of Stilwell et al. (1976) suggests that a physical mechanism of habitat alteration may change the character of benthic populations in quiescent waters. The mechanism of this effect has been discussed in Section III.

V. Criteria Formulation

Nitrocellulose is a stable organic compound capable of persisting unaltered in the environment for an undetermined period of time. Nitrocellulose was found to reduce the growth of green alga, Selenastrum capricornutum,

after 96 hours continuous exposure to concentrations as low as 114 mg/l. The 96-hour EC50 of this algae species was estimated at 731 mg/l with a 95 percent confidence interval of 475 mg/l - 1,039 mg/l. The mechanism involved, however, was not determined, but was probably due to light attenuation rather than chemical toxicity. Concentrations of up to 1,000 mg/l in the water column were not acutely toxic to fish or invertebrates. Concentrations up to 540 mg/kg in sediment were not toxic to midges. Cellulose trinitrate apparently cannot be metabolized. Ellis et al. (1976) found that this compound was nontoxic to mammals and was not adsorbed or broken down by several species. This compound also is not degraded by bacteria and probably is not chemically toxic to microbial life. Nitrocellulose therefore probably does not produce direct toxic effects on aquatic organisms.

The particulate nature of nitrocellulose wastes, the compound's relative insolubility in water, as well as its observed ability to attenuate light transmission through a suspension medium, indicate that current EPA water quality criteria for solids and turbidity are sufficient to provide for safe levels of nitrocellulose in the aquatic environment. These criteria (EPA 1976) suggest for the protection of freshwater fish and aquatic life:

> Settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life.

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